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14. ABSTRACT

The preparation, reactivity, and synthetic applications of functionalized perfluorooctynyl and fluorooctenyl silanes were explored. Fluorinated compounds are unique in that they are water and oil repellent, lubricative, incombustible, and chemically inert. Fluorinated silsesquioxanes have attracted considerable attention from material scientists as they provide nano-scaffolds for the fluoroalkyl groups. One route to *perfluorinated* silsesquioxanes is via condensation of an alkynyltrialkoxysilane or alkynyltrihalosilane. In this work, a *perfluorinated* alkynyl silane monomer represented by the formula R_fSiX_3 [R_f = perfluorooctyne group, X = OC_2H_5] was synthesized in 50% yield by nucleophilic addition of 1-perfluorooctynyl magnesium bromide with commercially available alkoxysilane electophiles. Unfortunately, acid hydrolysis leads to an ill-defined silsesquioxane mixture. Therefore, an alternative route was pursued using a *fluorooctenyl* silane. The unsaturated C-C double bond also provides a possible site of reactivity which could be used to attach the fluoro-POSS to surfaces, thereby increasing its durability. The synthesis of functionalized *fluorooctenyl* silane and its condensation reactions will be discussed.

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Introduction

Fluorinated compounds are useful in organic chemistry because of their pharmaceutical, agrochemical, and materials science applications.[1, 2] There is growing interest in new synthetic routes to produce such materials as well as in gaining a better understanding of their reactivity. Fluorosilicone materials, containing long-chain fluoroalkyl groups, possess many useful properties found in both silicones and fluoropolymers.[3] Fluorosiloxanes typically exhibit excellent solvent-resistance, thermal stability, weathering properties, and wear resistance. They also have surface energy values as low as 7.0 mN/m[4]

The first practical synthesis of organosilanes was accomplished by Kipping in 1904 using a Grignard reaction.[5] For practical purposes, alkoxy- and chloro-silanes are the most convenient precursors to alkynylsilanes because an alkynyl Grignard or lithium reagent can easily displace a chloro or alkoxy group. The Grignard reaction with alkoxysilanes is very general and found to be more selective than analogous reactions with chlorosilanes.[6] This results from stepwise substitution at the silicon atom. Substitution can be controlled by variation in reagent ratios as well as reagent reactivity. Multiple substitutions are favored when the activation energy for sequential substitution varies over a narrow range.[7] It has also been shown that the replacement of diethyl ether by toluene significantly accelerates the reaction of alkylmagnesium halides with alkoxysilanes, while no effect has been found for the same reaction with chlorosilanes.[8]

Fluorinated silsesquioxanes have attracted considerable attention in materials science.[9] Condensation of an alkynyltrialkoxysilane or alkynyltrihalosilane is a potential route to the synthesis of a *perfluorinated* silsesquioxane. Several attempts to synthesize and isolate pure perfluorooctynyltrihalosilane resulted in formation of new tetrakis perfluorooctynyl silane. Therefore, methods were devised to produce previously unreported perfluoroalkynyltriethoxysilane. and vinylfluoroalkenyltriethoxysilane. The stability of the alkynyl-silcon bond and alkenyl-silicon bond under condtions of hydrolysis will determine if it is possible to produce the desired fluorinated polyhedral oligomeric silsesquioxanes or silsesquioxane networks.[10] Such materials would be of interest as surface property modifiers to a host of polymeric systems.

Experimental

Instrumentation. ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker 300 or 400 MHz spectrometer using 5 mm o.d. NMR tubes and $CDCl_3$ and C_6F_6 as the internal reference standards (^{1}H: $CHCl_3$ at 7.26 ppm; ^{13}C: $CDCl_3$ at 77.23 ppm; ^{19}F: C_6F_6 at -163.8 ppm). Tetramethylsilane at 0 ppm was used for ^{29}Si as an external standard.

Materials. 1H-Perfluorooct-1-yne and hexafluorobenzene were purchased from Synquest Laboratories and used without further purification. Ethylmagnesium bromide solution, tetraethyl orthosilicate (TEOS), tetrachlorosilane, chlorotriethoxy silane, triethoxysilane, anhyd. ethanol, ammonium hydroxide (28-30% NH_3) and karstedt's catalyst were purchased from Aldrich Chemical Co. AK225 was obtained from AGC Chemicals Americas Inc. Gl. acetic acid was obtained from Military supply agency. Anhydrous diethyl ether, THF, and toluene (Aldrich) were dried by passage through columns of activated alumina under a nitrogen atmosphere. The solvents were degassed prior to use. All reactions were carried out under an inert atmosphere of dry N_2 unless otherwise stated in the procedure. Manipulations of all compounds and anhydrous solvents were carried out using standard Schlenk line techniques.

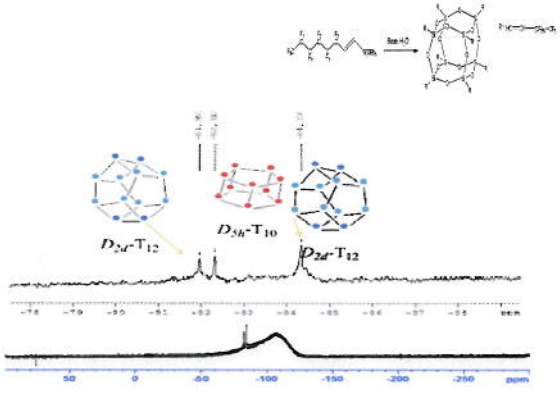
Synthesis of triethoxysilylperfluorooctyne: A solution of ethylmagnesium bromide (5 mmol) in 5 mL of anhydrous THF was taken in an addition funnel and slowly added to a stirring solution of 1H-perfluorooctyne (5 mmol) in anhydrous ethereal solution. The reaction was allowed to stir for approximately 2 h at ambient temperature and canulated into a stirring solution of tetraethyl orthosilicate (15 mmol) in ethereal solvent. The above mixture was stirred overnight, following which, solvent was removed *in vacuo* from the reaction mixture. Hexafluorobenzene was then added to the residual viscous product and the solution filtered through celite. After removing all volatiles under a dynamic vacuum, the yellow filtrate was transferred to a distillation flask. The product, perfluoro-1-octynltriethoxysilane was obtained by fractional distillation under reduced pressure as a colorless liquid in 50% yield. ^{1}H NMR ($CDCl_3$) δ 3.88 ppm (q, 6H, O-CH_2); 1.26 (t, 9H, CH_3) ^{13}C NMR δ 92.16 (t, J_{CC}=71 Hz, $\equiv C(CF_2)_5$); 87.43 (t, J_{CC}=10 Hz, $\equiv C$-$Si(OCH_2CH_3)_3$); 59.80 (OCH_2); 17.96 (CH_3CH_2O); ^{19}F NMR δ -80.89 ppm (3F), -98.43 ppm (2F), -120.36 ppm (2F), -122.17 ppm (4F), -125.70 ppm (2F); ^{29}Si NMR δ -78.06 ppm. Elemental analysis calcd for $C_{14}H_{15}F_{13}O_3Si$: C, 33.21; H, 2.99; F, 48.78. Found: C, 33.28; H, 3.03; F, 48.60.

Synthesis of vinylperfluorooctenyltriethoxysilane: In the glove box, 1H-perfluorooctyne (20 mmol) was slowly added to a stirring mixture of Karstedt's catalyst (octyne:catalyst= 5000:1) and triethoxysilane (22 mmol) in a pressure vessel and sealed. The reaction was then allowed to stir for approximately three days at 60 °C in an oil bath. After removing all volatiles under dynamic vacuum, the yellow filtrate was transferred to a distillation flask. The product, **vinylperfluorooctenyltriethoxysilane** was obtained by distillation under 20 torr partial pressure as a colorless liquid in 65% yield. ^{1}H NMR ($CDCl_3$) δ.6.48-6.30 ppm (m,$^{3}J_{HH}$=18 Hz, *trans*, HC=HC,), 3.86 ppm(q, 6H, O-CH_2); 1.25 ppm (t, 9H, CH_3); ^{13}C NMR δ 135.06 (t, J_{CC}=50 Hz, $=C(CF_2)_5$); 133.56(t, J_{CC}=15 Hz, $=C$-$Si(OCH_2CH_3)_3$); 59.80 (OCH_2); 17.96 (CH_3CH_2O);^{19}F NMR δ -81.19 ppm (3F), -105.34.ppm (2F), -114.30.ppm (2F), -123.55 ppm (4F), -126.42 ppm (2F). ^{29}Si NMR δ -61.77ppm

Hydrolysis and Condensation of vinylperfluorooctenyltriethoxysilane:

To a 1M solution of vinylperfluorooctenyltriethoxysilane (5 mmol, 1.90 mL) in 50:50 mixture of AK225 (1.4825 mL) and anhyd. ethanol (1.4825 mL), was added 7.5 mmol (0.135 mL) of DI water and catalytic amount (0.015 mmol, 0.9µL) of gl. acetic acid. The pressure vessel was crimped and the reaction was stirred at 40 °C in an oil bath for one day. This was followed by addition of catalytic amount (0.03 mmol, 13.63 µL) of ammonium hydroxide (28-30% content NH_3) and stirred again for three days at 40 °C in an oil bath. The product was extracted with hexafluorobenzene, washed with DI water and separated. The organic layer was pumped to dryness and a clear viscous liquid was obtained. ^{29}Si NMR (C_6F_6) δ, -82.31 ppm (T10), -81.95ppm, -84.33ppm(1:2,T12).

Fig 1: ^{29} Si Spectra of Acid-Base Hydrolytic condensation of vinylperfluorooctenyltriethoxy silane



Results and Discussion

One route to *perfluorinated* silsesquioxanes is *via* condensation of an alkynyltrialkoxysilane or alkynyltrihalosilane. Traditionally, the synthesis of alkoxy silanes has been accomplished by the treatment of Grignard or organo-lithium reagents with either $SiCl_4$ (followed by alcoholysis),[11] Cl-Si$(OR)_3$[12] or Si$(OR)_4$.[13] The use of Si$(OR)_4$ for the one-step preparation of alkoxysilanes *via* the organometallic approach has shown to have several advantages, including the commercial availability, low cost, and ease of handling and storage of tetraalkyl orthosilicates.[14] Treatment of alkynyl-metalloids with a less reactive electrophile, Si$(OEt)_4$, favors the formation of monoalkynyl silanes because the alkoxide group is more difficult to displace from silicon than a chloride atom.[15] The drawback of using reactive $SiCl_4$ as an electrophile include the formation of tetrakis(perfluoroalkynyl)silane species and the two step conversion to alkoxy silane. Treatment of the alkynylmetalloid with Cl-Si $(OR)_3$ favored the formation of monoalkynyl silane by preferential displacement of chloride from silicon. However, formation of inseparable di- and tri-alkynyl silanes also takes place under these conditions. In this work, a *perfluorinated* alkynyl silane monomer represented by the formula R_fSiX_3 [R_f = perfluorooctyne group, X=OC_2H_5] was synthesized in 50% yield by nucleophilic addition of 1-perfluorooctynyl magnesium bromide with commercially available alkoxysilane electophiles. 1-perfluorooct-1-ynylmagnesium bromide was selected as the initial nucleophile to be investigated in the metalation procedure. Grignard reagents have been reported to have significantly lower reactivity than the lithium reagents, which rapidly decompose at ambient temperatures. The inexpensive, commercially available electrophile tetraethyl orthosilicate, chlorotriethyl orthosilicate and tetrachlorosilane were each evaluated for their efficacy in formation of the Si-C≡C moiety. Ether, THF, and THF/toluene were evaluated for their suitability in the silylation of alkynylmagnesium bromide intermediate. Unfortunately, acid hydrolysis of perfluorooctynylsilane monomer leads to an ill-defined silsesquioxane product mixture. The Si-C bond adjacent to C≡C bonds is stable under sol-gel conditions, but is susceptible to cleavable by chemical treatment.[16] This challenge was, therefore, overcome by using an alternative route using vinylper*fluorooctenyl* silane. A two-step acid-base catalyzed process was employed for the preparation of homogeneous hybrid organic/inorganic sols. Acid-base hydrolytic condensation of the vinylperfluorooctenyl silane monomer led to the production of clearly identifiableT10 and T12 cages of vinylperfluorooctenyl POSS. This new type of POSS may exhibit even lower surface energy values compared the dodecyl-fluoro-POSS that recently was shown to have the lowest surface for any discreet molecule.[9] Additionally, vinylperfluorooctenyl POSS contains a reactive chemical functionality that may be utilized to produce new types of fluoro-POSS containing polymers, or to bind the fluoro-POSS to surfaces through chemical bonding, thereby increasing its durability.

Conclusions:

In the current work, novel fluorosilane monomers, perfluorooctynylsilane and vinylper*fluorooctenyl* silane were synthesized Perfluorooctynylsilane was synthesized *via* a Grignard reaction, followed by substitution between perfluorooct-1-ynyl magnesium bromide and alkoxysilanes. The product formation and reactivity rate is a function of molar ratios of reactants used and solvent polarity. It was determined that the substitution reactions can proceed efficiently and in a controlled manner when the solvent polarity is controlled. The reaction temperature did not influence the product yield, which is contrary to the chemistry of non-fluorinated analogues. Acid hydrolysis of perfluorooctynylsilane monomer leads to an ill-defined silsesquioxane mixture. Vinylper*fluorooctenyl* silane was synthesized via hydosilation of 1H-perfluorooctyne Acid-base hydrolytic condensation of the vinylperfluorooctenyl silane monomer led to the production of clearly identifiableT10 and T12 cages of. vinylperfluorooctenyl POSS.

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References

1. Filler, R.; Koayashi, Y. *Biomedical Aspects of Fluorine Chemistry;* Kodasha/Elsevier: New York, **1982**.
2. Banks, R.E. *Organofluorine Chemistry:Principles and Commercial Applications*; Plenum Press:New York, **1994**.
3. Guida-Pietrasanta, F.; Boutevin, B.; Nuyken, O. *Inorganic Polymeric Nanocomposites and Membranes, Advances in Polymer Science*, **2005**,179
4. Kobayashi, H.; Owen, M. J. *Die Makromol. Chem.* **1993**, *194*, 259.
5. Kipping, F. S. *Proc. Chem. Soc., London* **1904**, *20*, 15.
6. Brook, M.A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000.
7. Tuulmets, A.; Ploom, A.; Panov, D.; Jarv, J. *Synlett* **2010**, *No. 2*, 291.
8. Tuulmets, A.; Nguyen, B.T.; Panov, D.; Sassian, M.; Jarv, J. *J. Org. Chem.* **2003**, *68*, 9933.
9. Tuteja, A.; Choi, W.; Ma, M.; Mabry, J.; Mazzella, S.; Rutledge, G.; Mckinley, G.; Cohen, R. *Science* **2007** 318, 1618
10. Ameduri, B.;Boutevin, B.; Moreau, Joel J.E.; Moutaabbid, H.; Chi Man, M.W. *Journal of Fluorine Chemistry*, **2000**, *104*, 185.
11. Shibata, K.; Miyazawa, K.; Goto, Y. *J. Chem. Soc., Chem. Commun.* **1997**, *14*, 1309.
12. Cerveau, G.; Chappellet, S.; Corriu, R. J. P.; Dabiens, B. *J.Organomet. Chem.* **2001**, *626*, 92.
13. Corriu, R. J. P.; Mix, A.; Lanneau, F. G. *J. Organomet. Chem.* **1998**, *570*, 183.
14. Blomberg, C. *The Barbier Reaction and Related One-Step Processes*, 1st ed.; Springer-Verlag: Heidelberg, **1993**.
15. Amy S. Manoso, Chuljin Ahn, Arash Soheili, Christopher J. Handy, Reuben Correia, W. Michael Seganish, and Philip DeShong. *J. Org. Chem.* **2004**, *69*, 8305.
16. Yasuhiro Fujimoto, Atsushi Shimojima and Kazuyuki Kuroda. *J. Mater. Chem.* **2006**, *16*, 986